



(19)

Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 0 947 351 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
25.09.2002 Bulletin 2002/39

(21) Application number: 98947898.7

(22) Date of filing: 15.10.1998

(51) Int Cl.7: **B41M 5/26, G11B 7/24**

(86) International application number:  
PCT/JP98/04675

(87) International publication number:  
WO 99/020472 (29.04.1999 Gazette 1999/17)

**(54) MEMORY MEMBER**

**SPEICHERUNGSELEMENT**

**DISPOSITIF A MEMOIRE**

(84) Designated Contracting States:  
DE

(30) Priority: 17.10.1997 JP 28567097

(43) Date of publication of application:  
06.10.1999 Bulletin 1999/40

**(73) Proprietors:**

- Kabushiki Kaisha Toyota Chuo Kenkyusho  
Aichi-gun, Aichi-ken, 480-1192 (JP)
- Denso Corporation  
Kariya-city, Aichi-pref., 448-8661 (JP)

**(72) Inventors:**

- FUKANO, Tatsuo K. K. Toyota Chuo Kenkyusho,  
Aichi-gun Aichi-ken 480-1192 (JP)
- TAKEDA, Yasuhiko,  
K. K. Toyota Chuo Kenkyusho,  
Aichi-gun Aichi-ken 480-1192 (JP)
- KATO, Naohiko, K. K. Toyota Chuo Kenkyusho,  
Aichi-gun Aichi-ken 480-1192 (JP)

- MOTOHIRO, Tomoyoshi ,  
K. K. Toyota Chuo Kenkyusho  
Aichi-gun Aichi-ken 480-1192 (JP)

**(74) Representative:**

Blumbach, Kramer & Partner GbR  
Radeckestrasse 43  
81245 München (DE)

**(56) References cited:**

JP-A- 2 215 587                      JP-A- 3 258 590  
JP-A- 54 133 134                    JP-A- 57 208 299  
JP-A- 60 099 699

- DATABASE WPI Section Ch, Week 8550 Derwent  
Publications Ltd., London, GB; Class A89, AN  
85-314063 XP002110437 & JP 60 219097 A (FUJI  
PHOTO FILM CO LTD), 1 November 1985  
(1985-11-01)
- PATENT ABSTRACTS OF JAPAN vol. 017, no.  
149 (P-1509), 24 March 1993 (1993-03-24) & JP 04  
319545 A (NOBUYOSHI KOSHIDA; OTHERS: 01),  
10 November 1992 (1992-11-10)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

## Description

### Technical Field

[0001] The present invention relates to a recording medium which comprises a first substance and a second substance at least, and in which an external energy is applied to at least one of the first and second substances to react with each other, thereby varying their optical characteristics to record information.

### Background Art

[0002] Conventionally, there has been proposed a recording medium which includes a first substance and a second substance, and in which the first and second substances cause an oxidation-reduction reaction by being irradiated with an external energy, for example, a laser beam, thereby varying the optical characteristic to record information.

[0003] For example, U. S. Patent No. 5,459,018 discloses a recording medium in which metal, such as Al and Fe, is used as a first substance, and oxide, such as  $\text{TeO}_2$  and  $\text{In}_2\text{O}_3$ , is used as a second substance. These substances coexist to make a single-layered film, or are laminated alternately to make a laminated film.

[0004] By the way, according to the investigation carried out by the inventors of the present invention, when the recording medium utilizes the oxidation-reduction reaction between the first substance and the second substance as set forth in the aforementioned prior art, the reaction of the first and second substances develop in the middle of the film formation because the first and second substances both have reactivities. As a result, there arises a possibility of decreasing overall reflectance. Further, in such a recording medium, the first and second substances react with each other when the external energy is not applied (when information is not recorded). Thus, it is expected that the retention of the recorded information deteriorates due to chronological degradation. In an actual application, it is believed that there arise problems when the recording medium is used as an ordinary recording medium.

[0005] Furthermore, according to the further investigation carried out by the inventors of the present invention, in order to obtain high reflectance, it is necessary to use a substance of good reflectance as a substance which carries out the reaction when the external energy is applied (when information is recorded). However, because of the good reflectance, the substance exhibits small absorptance to the external energy. As a result, the substance absorbs less heat which is required for the reaction, because it is of good reflectance. Accordingly, it is preferred that the first and second substances are a combination which shows good reactivity when information is recorded. However, the combination showing good reactivity causes unnecessary reactions when the films are formed as aforementioned or when infor-

mation is not recorded. Thus, the possibility increases in that the recording characteristics of the recording medium degrade.

[0006] The present invention has been developed in view of the aforementioned problems. Therefore, in a recording medium which includes a first substance and a second substance at least, the first and second substances undergoing an oxidation-reduction reaction when an external energy is applied thereto, thereby recording information by varying the optical characteristics, it is therefore an object of the present invention to suppress the reaction of the first and second substances, reaction which degrades the recording characteristics other than the case where the recording medium is subjected to recording.

### Disclosure of Invention

[0007] While investigating into a recording medium which includes a first substance and a second substance at least, and which record information by varying the optical characteristics by applying an external energy, the present invention has been completed by elaborating the combination of the first substance and the second substance which undergo an oxidation-reduction reaction, and by diligently studying a third substance which suppresses the reactivities of the first and second substances.

[0008] The present recording medium is characterized in that it is a recording medium for recording information by varying optical characteristics thereof by applying an external energy thereto, which includes:

a first substance and a second substance which cause an exothermic reaction to vary optical characteristics of said first and second substances when the external energy is applied, said first substance undergoing oxidation in a wide sense; and said second substance undergoing reduction in a wide sense; and  
a third substance interposed between said first substance and said second substance, enabling said first substance and said second substance to react when said external energy is applied, and suppressing said first substance and said second substance to react when said external energy is not applied.

[0009] When the external energy is applied to the present recording medium, the first substance reduces the second substance with the first substance and the second substance passing through the third substance and/or destroying the third substance. And, the first substance itself undergoes the oxidation in a wide sense. Thus, the first substance and the second substance undergo an oxidation-reduction reaction. Due to the reaction, at least a part of the first and second substances vary the optical characteristics, and thereby information

is recorded in the present recording medium.

[0010] Then, since the third substance is interposed between the first substance and the second substance, the aforementioned oxidation-reduction reaction is suppressed when forming films or when the external energy is not applied (when information is not recorded).

[0011] Further, since the oxidation-reduction reaction is an exothermic reaction, the resulting modified reaction products are stable energetically, and the reverse reaction is less likely to occur. Hence, the present recording medium can suppress the reaction between the first and second substances which degrades the recording characteristics.

[0012] Said first substance can be at least one member selected from the group consisting of metals, intermetallic compounds, nitrides, carbides, silicides, borides, sulfides, selenides, tellurides, phosphides, arsenides, antimonides and substances containing these members. The members generate an energy of 1,000 kJ or more when bonding with oxygen molecules in an amount of 1 mol (hereinafter referred to as an "oxygen-bonding energy"), and contain at least one element selected from the group consisting of elements of group 1 of the periodic table of the elements, elements of group 2 thereof, elements of group 3 thereof, elements of group 4 thereof, elements of group 5 thereof, Cr, Mn, Zn, Al and Si.

[0013] The elements of group 1 can be Li, Na, K, etc. The elements of group 2 can be Mg, Ca, etc. The elements of group 3 can be Sc, Y, etc. The elements of group 4 can be Ti, Zr, etc. The elements of group 5 can be V, Nb, etc.

[0014] Said second substance can be at least one member selected from the group consisting of oxides, substances containing oxygen as a constituent element, substances with oxygen adsorbed, compounds thereof or mixtures thereof. The members require an energy of 550 kJ or less when dissociating oxygen molecules in an amount of 1 mol (hereinafter referred to as an "oxygen-dissociating energy").

[0015] The second substance gives oxygen to the first substance to oxidize it, and is itself likely to be reduced. The second substance can be a substance containing at least one member selected from the group consisting of oxides and substances containing oxygen as a constituent element. The members contain at least one element selected from the group consisting of elements of group 6 of the periodic table of the elements, elements of group 8 thereof, elements of group 9 thereof, elements of group 11 thereof, Ti, V, Mn, Ni, Re, Ge, Sn, Pb, As, Sb, Bi, Se, Te, Ce, Pr and Tb.

[0016] Here, the elements of group 6 can be Cr, Mo, etc. The elements of group 8 can be Fe, Ru, etc. The elements of group 9 can be Co, Rh, Ir, etc. The elements of group 11 can be Cu, Ag, Au, etc.

[0017] According to the investigations carried out by the inventors of the present invention, when the oxygen-bonding energy of the first substance is less than 1,000

kJ, the first substance is less likely to bond with the oxygen, and the reactivity decreases. Moreover, when the oxygen-dissociating energy of the second substance is more than 550 kJ, the oxygen is less likely to dissociate, and the reactivity decreases. Accordingly, the first and second substance can preferably have the aforementioned respective energy ranges.

[0018] Further, the first substance can be a substance containing at least one member selected from the group consisting of metals, intermetallic compounds, nitrides, carbides, silicides, borides, sulfides, selenides, tellurides, phosphides, arsenides, antimonides and substances containing these members. The members generate an oxygen-bonding energy of 500 kJ or more, and exhibit a melting point or a decomposition temperature of from 100 °C or more to 300 °C or less. And, the second substance can be a substance containing at least one member selected from the group consisting of oxides, substances containing oxygen as a constituent element, substances with oxygen adsorbed, compounds thereof and mixtures thereof. The members require an oxygen-dissociating energy of 550 kJ or less.

[0019] Furthermore, the second substance gives oxygen to the first substance to oxidize it, and is itself likely to be reduced. The second substance can be a substance containing at least one member selected from the group consisting of oxides and substances containing oxygen as a constituent element. The members contain at least one element selected from the group consisting of elements of group 6 of the periodic table of the elements, elements of group 8 thereof, elements of group 9 thereof, elements of group 11 thereof, Ti, V, Mn, Ni, Re, Ge, Sn, Pb, As, Sb, Bi, Se, Te, Ce, Pr and Tb.

[0020] Here, the elements of group 6 can be Cr, Mo, etc. The elements of group 8 can be Fe, Ru, etc. The elements of group 9 can be Co, Rh, Ir, etc. The elements of group 11 can be Cu, Ag, Au, etc.

[0021] By having the first substance exhibit a melting point or a decomposition temperature in the aforementioned range, the first substance can be turned into a liquid phase by a small external energy. The aforementioned oxidation-reduction reaction is a reaction between the liquid phase and the solid phase so that the reactivity is enhanced compared with the reaction between the solid phases. When the substance constituting the first substance exhibits a melting point or a decomposition temperature of less than 100 °C, the heat resistance of recorded data decreases. When the melting point or the decomposition temperature exceeds 300 °C, a large external energy is required unpreferably.

[0022] Moreover, by having the first substance exhibit a melting point or a decomposition temperature in the aforementioned range, the reactivity is enhanced. Accordingly, the oxygen-bonding energy of the first substance can be decreased, and is 500 kJ or more. According to the investigations carried out by the inventors of the present invention, when the oxygen-bonding energy is less than 500 kJ, the reactivity is decreased un-

preferably.

[0023] Note that, even when the third substance is interposed, the first substance and the second substance cause the oxidation-reduction reaction, at least a part of the first and second substances are modified to vary the optical characteristics. Thus, information is recorded. And, even when the first substance and the second substance are made into the aforementioned combination of good reactivity, the interposing third substance can suppress the reaction between the first and second substances, reaction which degrades the recording characteristics other than the case where the recording medium is subjected to recording.

#### Brief Description of Drawings

[0024] Fig. 1 is an explanatory diagram for illustrating the cross-sectional arrangement of an optical disk according to preferred embodiments of the present invention.

[0025] Fig. 2 is a table for summarizing the recording characteristics of optical disks of a First Preferred Embodiment and a comparative example.

[0026] Fig. 3 is a table for summarizing the recording characteristics of optical disks of a Second Preferred Embodiment and a comparative example.

[0027] Fig. 4 is a table for summarizing the recording characteristics of optical disks of a Third Preferred Embodiment and a comparative example.

#### Best Mode for Carrying Out the Invention

##### (First Preferred Embodiment)

[0028] A recording medium of this First Preferred Embodiment is directed to recording information by varying a recording film physically and/or chemically by irradiating it with a recording laser beam as an external energy. For example, it is applicable to an optical disk in which music or data is recorded as information. Fig. 1 illustrates a partial cross-sectional construction of an optical disk (recording medium) 100 of this preferred embodiment.

[0029] An optical disk 100 is formed as a disk as a whole, and a plurality of layers are formed and laminated as illustrated in Fig. 1. 1 designates a transparent substrate which is formed as a disk (for example, in a thickness of 1.2 mm) and is made from polycarbonate, for instance. A laser beam for optically recording and reading out information enters from a surface 1a of the substrate 1 in the direction specified by the arrow "A". The surface 1a, the laser-beam-incidence side, is a flat surface, and on the other side 1b, there is formed a spiral or concentric guide groove (track) 1c for leading the laser beam.

[0030] On the other surface 1b of the substrate 1, there is formed a  $WO_3$  film 2, including  $WO_3$  (a second substance), as a second layer. And, on the  $WO_3$  film 2,

there is formed a C film (carbon film) 3, including carbon (a third substance), as a barrier layer (third layer). On the C film 3, there is formed an Sn-10 atomic % Sr film 4, including Sn-10 atomic % Sr (a first substance), as a first layer. The C film 3 has a thickness (for example, 1 nm or more) which is appropriate for suppressing the physical and/or chemical reaction between the  $WO_3$  film 2 and the Sn-10 atomic % Sr film 4.

[0031] Here, the aforementioned films 2, 3 and 4 constitute a recording film 10 in the optical disk 100. Moreover, on the Sn-10 atomic % Sr film 4, there is formed a resin film (protective film) 5 which covers the recording film 10 to protect it and includes an ultraviolet-curable resin.

[0032] Next, the manufacturing method of the optical disk 100 will be described in detail.

[0033] The substrate 1 was prepared. The opposite surface 1a was formed as a flat surface. In the other surface 1b, there was formed the guide groove 1c. The substrate 1 was composed of a disk having a thickness of 1.2 mm, and was made from polycarbonate. On the other surface 1b of the substrate 1, the  $WO_3$  film 2 was formed in a thickness of 185 nm by an RF magnetron sputtering method with a  $WO_3$  target under the following film forming conditions of sputtering gas species: Ar + 10%  $O_2$ , sputtering gas pressure: 0.533 Pa ( $4 \times 10^{-3}$  Torr) and input electric power: 100 - 400 W. Subsequently, the C film 3 was formed in a thickness of 2 nm by an RF magnetron sputtering method with a C (graphite) target under the following film forming conditions of sputtering gas species: Ar, sputtering gas pressure: 0.533 Pa ( $10^{-3}$  Torr) and input electric power: 200 - 500 W.

[0034] Still subsequently, the Sn-10 atomic % Sr film 4 was formed in a thickness of 35 nm by an RF magnetron sputtering method with an Sn-10 atomic % Sr target under the following film forming conditions of sputtering gas species: Ar, sputtering gas pressure: 0.533 Pa ( $4 \times 10^{-3}$  Torr) and input electric power: 50 - 200 W.

[0035] Finally, the ultraviolet-curable resin was applied by a spin coating method, the ultraviolet-curable resin was cured using a high-pressure mercury-vapor lamp to form the resin film 5 and thus, the optical disk 100 was manufactured.

[0036] The recording actions of the optical disk 100 of this preferred embodiment are as hereinafter described. In the portion of the guide groove 1c, the recording laser beam enters (irradiates) in the direction of the arrow "A", and is focused on the surface of the Sn-10 atomic % Sr film 4. Further, the  $WO_3$  film 2 and the Sn-10 atomic % Sr film 4 undergo a chemical reaction with the  $WO_3$  and the Sn-10 atomic % Sr passing through the C film 3 and/or destroying the C film 3. Accordingly, when the recording laser beam is irradiated (when the external energy is applied), the optical characteristics (reflectance, etc.) of the recording film vary so that information can be recorded.

[0037] When the recording laser beam is not irradiated (when the external energy is not applied), since the

C film 3 is interposed between the  $\text{WO}_3$  film 2 and the Sn-10 atomic % Sr film 4, the reaction between the  $\text{WO}_3$  film 2 and the Sn-10 atomic % Sr film 4 is suppressed, and as a result, the recording characteristics can be inhibited from degrading.

[0038] The reaction between the  $\text{WO}_3$  film 2 and the Sn-10 atomic % Sr film 4 at this time is an oxidation-reduction reaction in a wide sense as hereinafter described. By irradiating with the recording laser beam, the  $\text{WO}_3$  (the second substance), forming the film 2, is reduced and a part of or all of it is turned into  $\text{WO}_{2.83}$ . The Sn-10 atomic % Sr (the first substance), forming the film 4, is oxidized and a part of or all of it is turned into SrO and/or SnO.

[0039] At this moment, the color hues of the substances constituting the films are as follows. The  $\text{WO}_3$  is transparent, the  $\text{WO}_{2.83}$  is blue, the Sn-10 atomic % Sr is metallic gloss, the SrO is transparent, and the SnO is gray. Accordingly, the optical characteristics of the optical disk 100 before and after recording vary greatly.

[0040] The energy required for the  $\text{WO}_3$  to dissociate oxygen molecules in an amount of 1 mol and to turn into the  $\text{WO}_{2.83}$  (oxygen-dissociating energy) is about 480 kJ at room temperature, while the energies generated by the Sr and the Sn to bond with oxygen molecules in an amount of 1 mol and to turn into the SrO and the SnO (oxygen-bonding energy) are about 1,220 kJ and 610 kJ, respectively, at room temperature. Therefore, the reaction between the  $\text{WO}_3$  film 2 and the Sn-10 atomic % Sr film 4 is an exothermic reaction.

[0041] And, in this preferred embodiment, since the oxidation-reduction reaction is an exothermic reaction, the modified reaction products ( $\text{WO}_{2.83}$ , SrO and SnO) are energetically stable, and the reverse reaction is less likely to occur. In addition, since the substances before the generation or after the generation are the oxides or the substance containing oxygen as a constituent element, they are strong against heat and moisture, etc., and are good in environmental resistance. Thus, when information is not recorded, it is likely to suppress the unnecessary reactions.

[0042] The specific example of the recording characteristics of this preferred embodiment will be described. In the optical disk 100 which was manufactured by the aforementioned manufacturing method, information was recorded by irradiating the optical disk with a laser beam (recording laser beam) of wavelength: 780 nm from the side of the flat surface (surface 1a), which was focused on the surface of the Sn-10 atomic % Sr film 4 through an objective lens of NA (numerical aperture): 0.5. At this moment, the irradiating conditions were linear velocity: 2.8 m/sec, recording frequency: 400 kHz and recording laser wave form: rectangular wave of 50% duty ratio.

[0043] The characteristics (recording characteristics) of the optical disk 100 in this instance were, as set forth in Sample No. 3 of Fig. 2, reflectance at unrecorded portions: 62%, recording laser power 10 mW, C/N (output-

level ratio of carrier to noise): 50 dB and modulation: 80%. Note that the modulation is a value which is obtained by subtracting the reflectance after the recording from the reflectance before the recording and dividing the difference by the reflectance before the recording.

[0044] Then, the optical disk characteristics as set forth above were measured by variously changing the thickness (in the drawing, denoted as "barrier layer thickness") of the C film 3 playing the role of the barrier layer (Sample Nos. 1, 2, 4 and 5), and Fig. 2 summarizes the results, together with the aforementioned results (Sample No. 3). Note that, in Fig. 2, Sample No. 6 was a comparative example to the present invention, and was free from the barrier layer.

[0045] As set forth in Fig. 2, it is understood that the optical disks 100 of this preferred embodiment listed as Sample Nos. 1 through 5 exhibited remarkably higher reflectance than the optical disk of the comparative example (Sample No. 6), and that they were well balanced in terms of the characteristics, such as the reflectance, the recording power, the C/N and the modulation. This results from the arrangement that the reaction between the first layer, the Sn-10 atomic % Sr film 4, and the second layer, the  $\text{WO}_3$  film 2, is suppressed by the presence of the C film 3.

[0046] Moreover, the respective optical disks of Sample Nos. 1 through 6 were subjected to an environmental resistance test which was carried out at 55 °C for 96 hours. The optical disks of this preferred embodiment could read out the recorded data. Whereas, it was impossible for the optical disk of the comparative example to read out the recorded data. This results from the arrangement that the reaction between the  $\text{WO}_3$  film 2 and the Sn-10 atomic % Sr film 4 is suppressed by the presence of the C film 3.

[0047] As described so far, the optical disks 100 of this preferred embodiment are characterized in that they are better balanced in terms of the characteristics, such as the reflectance, the recording power, the C/N and the modulation, than the conventional optical disk.

[0048] Moreover, in this preferred embodiment, the C film 3 is interposed between the  $\text{WO}_3$  film 2 and the Sn-10 atomic % Sr film 4. Accordingly, the reaction is suppressed in the formation of the films, under ordinary environment, and under the high-temperature-and-high humidity conditions such as the aforementioned environmental resistance test. Namely, the reaction is suppressed other than the case where information is recorded, and thus, the recording characteristics (reflectance, recording power, C/N and modulation) can be inhibited from degrading, and the data retention characteristic can be improved greatly. In addition, the reflectance (initial reflectance) at the unrecorded portions of the optical disk can be heightened remarkably.

[0049] By the way, the first and second substances according to the present invention are not limited to the substances of the aforementioned preferred embodiment.

[0050] Under the conditions that, the first substance and the second substance make a combination so that a first substance undergoes oxidation in a wide sense and a second substance undergoes reduction, thereby causing an exothermic reaction when an external energy is applied; and that at least a part of the first substance and/or the second substance have varied the optical characteristics before and after the exothermic reaction, the following substances can be employed.

[0051] The first substance can be any substance which reduces the second substance by retrieving or the like oxygen from the second substance, and is itself likely to be oxidized. Such a first substance can consist of one member selected from the group consisting of metals, intermetallic compounds, nitrides, carbides, silicides, borides, sulfides, selenides, tellurides, phosphides, arsenides, antimonides and compounds or mixtures thereof (13 kinds so far will be referred to as a substance group "P"), or alternatively, the first substance can be selected from substances containing at least one substance of the substance group "P".

[0052] In order to be more likely to bond with oxygen and in order to enhance the reactivity, the first substance can preferably be one substance of the substance group "P" which exhibits the oxygen-bonding energy of 1,000 kJ or more. For example, as the first substance, Sn-Sr alloys, Mg-Al alloys, In-Sr alloys, Al-Ti alloys, etc., which exhibit the oxygen-bonding energy of 1,000 kJ or more, can be employed (The oxygen-bonding energies are approximately Sn: 610 kJ, Sr: 1,220 kJ, Mg: 1,220 kJ, Al: 1,130 kJ, In: 640 kJ and Ti: 1,070 kJ.).

[0053] Further, in the aforementioned combination, the second substance can be any substance which oxidizes the first substance, and is itself likely to be reduced, or can alternatively be any substance which causes the first substance to undergo oxidation in a wide sense, in which the oxidation number is increased without directly exchanging oxygen atoms, and is itself reduced. And, the second substance can consist of one member selected from the group consisting of oxides, substances containing oxygen as a constituent element, substances with oxygen adsorbed and compounds or mixtures thereof (4 kinds so far will be referred to as a substance group "Q"), or alternatively, the second substance can be a substance containing at least one of the substance group "Q".

[0054] In order to be more likely to dissociate oxygen and in order to enhance the reactivity, the second substance can preferably be one substance of the substance group "Q" which exhibits the oxygen-dissociating energy of 550 kJ or less. For example, as the second substance,  $\text{MoO}_3$ ,  $\text{ReO}_2$ ,  $\text{PrO}_2$ ,  $\text{SbO}_2$ , etc., can be employed (The oxygen-dissociating energies are approximately  $\text{MoO}_3$ : 330 kJ,  $\text{ReO}_2$ : 450 kJ,  $\text{PrO}_2$ : 240 kJ and  $\text{SbO}_2$ : 380 kJ.).

[0055] In this preferred embodiment, as the third substance which is interposed between the first substance and the second substance, and which plays a role of

suppressing the reaction between the first and second substances other than the case where information is recorded, the following can be employed. First, the third substance can be oxides, such as  $\text{Al}_2\text{O}_3$ ,  $\text{SiAlON}$ , etc., substances containing oxygen as a constituent element, substances with oxygen adsorbed, or compounds thereof or mixtures thereof, which generate a quantity of heat in excess of 550 kJ when dissociating oxygen molecules in an amount of 1 mol. The substance, which generates a quantity of heat in excess of 550 kJ when dissociating oxygen molecules in an amount of 1 mol, can be preferable, because there is possibility that the reaction between the first substance and the second or third substance gradually develops when information is not recorded, if the substance generates a quantity of heat 550 kJ or less when dissociating oxygen molecules in an amount of 1 mol.

[0056] Further, the third substance can be an organic substance, such as  $\text{C}_m\text{H}_n$  (hydrocarbon),  $\text{C}_m\text{F}_n$ ,  $\text{C}_m\text{H}_n\text{F}_p$  or the like (m, n and p are integers), which exhibits a decomposition temperature (a decomposition, sublimation or melting temperature) of 300 °C or less. Among organic substances, the organic substance, which exhibits a decomposition temperature (a decomposition, sublimation or melting temperature) of 300 °C or less, can be preferable, because a laser beam power, which is applied when recording information, should be increased, if an organic substance exhibits a decomposition temperature of more than 300 °C, and thus, such an organic substance is not so practical for a recording medium.

[0057] Furthermore, the third substance can preferably be a substance which includes at least one member selected from the group consisting of metals, such as Mn, Ti, Se, Mn steels, titanium alloys, Si, Ge,  $\text{SiN}_x$ , etc., semiconductors, intermetallic compounds, nitrides, carbides, silicides, borides, sulfides, selenides, tellurides, phosphides, arsenides, antimonides and substances containing these members, which exhibit a thermal diffusion coefficient of 50  $\text{mm}^2/\text{sec}$  or less in bulk at room temperature. Among these substances, the substance, which exhibits a thermal diffusion coefficient of 50  $\text{mm}^2/\text{sec}$  or less in bulk at room temperature, can be preferable, because a laser beam power, which is applied when recording information, should be increased, if a substance exhibits a thermal diffusion coefficient of more than 50  $\text{mm}^2/\text{sec}$ , and thus such a substance is not so practical for a recording medium.

[0058] Moreover, the third substance can preferably exhibit a melting point, a decomposition temperature or a sublimation temperature of 1,000 °C or more in the case where it generates an energy of 1,000 kJ or more when bonding with oxygen molecules in an amount of 1 mol; or can exhibit a melting point, a decomposition temperature or a sublimation temperature of 300 °C or more in the case where it generates an energy of less than 1,000 kJ when bonding with oxygen molecules in an amount of mol. This is because there is a possibility that

the first substance reacts with the third substance when information is not recorded, especially when producing the recording medium, depending on the production conditions.

[0059] The thickness of the third substance layer can be selected so that it satisfies the required characteristics of the recording medium. However, the thickness can preferably be 0.5 nm or more in order to bring out the characteristics of the third substance as the barrier layer.

(Second Preferred Embodiment)

[0060] In the optical disk 100 illustrated in Fig. 1, this Second Preferred Embodiment differs from the recording medium of the aforementioned First Preferred Embodiment in that the first layer is an Sn-43 atomic % Bi film 40 instead of the Sn-10 atomic % Sr film, and in that the barrier layer is a hydrocarbon film 30 instead of the C film. The recording medium of this preferred embodiment operates and effects advantages in the substantially same manner as the recording medium of the aforementioned First Preferred Embodiment. Hereinafter, the portions, which differ from those of the recording medium of the First Preferred Embodiment, will be described mainly.

[0061] The manufacturing method of the recording medium of this preferred embodiment will be described with reference to a specific example.

[0062] On the surface 1b of the substrate 1, the WO<sub>3</sub> film 2 was formed in a thickness of 185 nm by an RF magnetron sputtering method with a WO<sub>3</sub> target under the following film forming conditions of sputtering gas species: Ar + 10% O<sub>2</sub>, sputtering gas pressure: 0.533 Pa (4 x 10<sup>-3</sup> Torr) and input electric power: 100 - 400 W.

[0063] Subsequently, the hydrocarbon film 30 was formed in a thickness of 2 nm by an RF magnetron sputtering method with a C (graphite) target under the following film forming conditions of sputtering gas species: Ar + 50% C<sub>3</sub>H<sub>8</sub> (propylene), sputtering gas pressure: 0.533 Pa (4 x 10<sup>-3</sup> Torr) and input electric power: 200 - 500 W. Still subsequently, the Sn-43 atomic % Bi film 40 was formed in a thickness of 45 nm by an RF magnetron sputtering method with an Sn-43 atomic % Bi target under the following film forming conditions of sputtering gas species: Ar, sputtering gas pressure: 0.533 Pa (4 x 10<sup>-3</sup> Torr) and input electric power: 50 - 200 W.

[0064] Finally, the ultraviolet-curable resin was applied by a spin coating method, and it was cured using a high-pressure mercury-vapor lamp to form the resin film 5, thereby obtaining the optical disk 100.

[0065] The recording actions of the optical disk 100 of this preferred embodiment are assumed to be as follows. In the portion of the guide groove 1c, the recording laser beam enters (irradiates) in the direction of the arrow "A", and is focused on the surface of the Sn-43 atomic % Bi film 40. Since the melting point of the Sn-43 atomic % Bi film 40 is as low as about 139 °C, a part

of or all of the Sn-43 atomic % Bi film 40, which is irradiated with the laser beam, melts, and in a certain case, holes are formed in the Sn-43 atomic % Bi film 40 in this instance.

[0066] Simultaneously therewith, the WO<sub>3</sub> film 2 and the Sn-43 atomic % Bi film 40, a part of or all of which melts, undergo a chemical reaction with the WO<sub>3</sub> and the Sn-43 atomic % Bi passing through the hydrocarbon film 30 and/or decomposing, sublimating, melting or destroying the hydrocarbon film 30. Accordingly, the optical characteristics (reflectance, etc.) of the recording film vary so that information can be recorded. Since the chemical reaction occurs between the molten liquid and the solid, the reaction occurs more easily than the case where the reaction occurs between a solid and the other solid.

[0067] When the recording laser beam is not irradiated, since the hydrocarbon film 30 is interposed between the WO<sub>3</sub> film 2 and the Sn-43 atomic % Bi film 40, the reaction between the WO<sub>3</sub> film 2 and the Sn-43 atomic % Bi film 40 is suppressed. As a result, the recording characteristics can be inhibited from degrading.

[0068] Note that the decomposition temperature (the decomposition, sublimation or melting temperature) of the organic substance used as the barrier layer (the hydrocarbon film 30 in this preferred embodiment) can preferably be 300 °C or less. When it is more than 300 °C, a laser beam power, which is applied when recording information, should be increased. Accordingly, such an organic substance is not so practical for a recording medium. According to the results of a thermal analysis, the decomposition temperature (the decomposition, sublimation or melting temperature) of the hydrocarbon film 30 used as the barrier layer in this preferred embodiment is assumed to fall in the range of from 100 to 200 °C.

[0069] Moreover, in the aforementioned preferred embodiment, an Al alloy containing Ti in an amount of less than 30 atomic % can be used as the first layer.

[0070] The reaction between the WO<sub>3</sub> film 2 and the Sn-43 atomic % Bi film 40 herein is also an oxidation-reduction reaction in a wide sense as hereinafter described. By irradiating with the recording laser beam, the WO<sub>3</sub> (the second substance), forming the film 2, is reduced, and a part of or all of it is turned into WO<sub>2.83</sub>. The Sn-43 atomic % Bi (the first substance), forming the film 40, is oxidized, and mainly a part of or all of Sn is chiefly turned into SnO.

[0071] At this moment, the color hues of the substances constituting the films are as follows. The WO<sub>3</sub> is transparent, the WO<sub>2.83</sub> is blue, the Sn-43 atomic % Bi is metallic gloss, and the SnO is gray. Accordingly, the optical characteristics of the optical disk 100 before and after recording vary greatly.

[0072] The energy required for the WO<sub>3</sub> to dissociate oxygen molecules in an amount of 1 mol and to turn into the WO<sub>2.83</sub> (oxygen-dissociating energy) is about 480 kJ at room temperature. The energy generated by the

Sn to bond with oxygen molecules in an amount of 1 mol and to turn into the SnO (oxygen-bonding energy) is about 610 kJ at room temperature. Therefore, the reaction between the WO<sub>3</sub> film 2 and the Sn-43 atomic % Bi film 40 is an exothermic reaction. By the way, the oxygen-bonding energy required for Bi to turn into Bi<sub>2</sub>O<sub>3</sub> is about 410 kJ at room temperature.

[0073] At this moment, in this preferred embodiment, compared with the aforementioned First Preferred Embodiment, the substance to be reduced, the Sn-43 atomic % Bi exhibits a much smaller oxygen-bonding energy than the Sn-10 atomic % Sr. Namely, the difference between the oxygen-bonding energy of the Sn-43 atomic % and the oxygen-dissociating energy of WO<sub>3</sub>, which is required for WO<sub>3</sub> to turn into WO<sub>2.83</sub>, is much smaller than the case of Sn-10 atomic % Sr. The reason, for which the similar recording action is induced even if the energy is less, is believed as follows.

[0074] Namely, when recording, a part of or all of the Sn-43 atomic % Bi, which exhibits a low melting point, melts, and in a certain case, holes are formed in the Sn-43 atomic % Bi film 40 in this instance. It is believed that, since the chemical reaction at this moment is a reaction between the molten liquid and the solid, the reaction occurs more easily than the case where the reaction occurs between a solid and the other solid.

[0075] Moreover, in this preferred embodiment as well, since the aforementioned oxidation-reduction reaction is an exothermic reaction, the modified reaction products (WO<sub>2.83</sub> and SnO) are stable energetically, and the reverse reaction is less likely to occur. In addition, since the substances before the generation or after the generation are the oxides or the substance containing oxygen as a constituent element, they are strong against heat and moisture, etc., and are good in environmental resistance. Thus, when information is not recorded, it is likely to suppress the unnecessary reactions.

[0076] The specific example of the recording characteristics of this preferred embodiment will be described. In the optical disk 100 which was manufactured by the aforementioned manufacturing method, information was recorded by irradiating with a laser beam (recording laser beam) of wavelength: 780 nm from the side of the flat surface (surface 1a), which was focused on the surface of the Sn-43 atomic % Bi film 40 through an objective lens of NA (numerical aperture): 0.5. At this moment, the irradiating conditions were linear velocity: 2.8 m/sec, recording frequency: 400 kHz and recording laser wave form: rectangular wave of 50% duty ratio.

[0077] The characteristics (recording characteristics) of the optical disk in this instance were, as set forth in Sample No. 12 of Fig. 3, reflectance at unrecorded portions: 63%, recording laser power: 7 mW, C/N: 52 dB and modulation: 85%.

[0078] Then, the optical disk characteristics as set forth above were measured by variously changing the thickness (in the drawing, denoted as "barrier layer

thickness") of the hydrocarbon film 30 playing the role of the barrier layer (Sample Nos. 11 and 13), and Fig. 3 summarizes the results, together with the aforementioned results (Sample No. 12). Note that, in Fig. 3, Sample No. 14 was a comparative example to the present invention, and was free from the barrier layer.

[0079] As set forth in Fig. 3, it is understood that the optical disks 100 of this preferred embodiment listed as Sample Nos. 11 through 13 exhibited remarkably higher reflectance than the optical disk of the comparative example (Sample No. 14), and that they were well balanced in terms of the characteristics, such as the reflectance, the recording power, the C/N and the modulation. This results from the arrangement that the reaction between the first layer, the Sn-43 atomic % Bi film 40, and the second layer, the WO<sub>3</sub> film 2, is suppressed by the presence of the hydrocarbon film 30.

[0080] Moreover, the respective optical disks of Sample Nos. 11 through 14 were subjected to an environmental resistance test which was carried out at 55 °C for 96 hours. The optical disks of this preferred embodiment could read out the recorded data. Whereas, it was impossible for the optical disk of the comparative example to read out the recorded data. This results from the arrangement that the reaction between the WO<sub>3</sub> film 2 and the Sn-43 atomic % Bi film 40 is suppressed by the presence of the hydrocarbon film 30.

[0081] As described so far, the optical disks 100 of this preferred embodiment are characterized in that they are better balanced in terms of the characteristics, such as the reflectance, the recording power, the C/N and the modulation, than the conventional optical disk.

[0082] Moreover, in this preferred embodiment, the hydrocarbon film 30 is interposed between the WO<sub>3</sub> film 2 and the Sn-43 atomic % Bi film 40. Accordingly, the reaction is suppressed in the formation of the films, under ordinary environment, and under the high-temperature-and-high humidity conditions such as the aforementioned environmental resistance test. Namely, the reaction is suppressed other than the case where information is recorded. Thus, the reflectance (initial reflectance) at the unrecorded portions of the optical disk can be heightened remarkably, and the recording characteristics (reflectance, recording powder, C/N and modulation) can be inhibited from degrading. In addition, the data retention characteristic can be improved greatly.

[0083] By the way, in this preferred embodiment as well, the first and second substances are not limited to the substances of the aforementioned example. Under the conditions that as far as the combination set forth in the aforementioned First Preferred Embodiment is satisfied, the following substances can be employed.

[0084] The first substance can be any substance which reduces the second substance by retrieving or the like oxygen from the second substance, and is itself likely to be oxidized. The first substance employed herein can be at least one substance of the substance group "P", exhibit an oxygen-bonding energy of 500 kJ or



more, and have a melting point or a decomposition temperature of from 100 °C or more to 300 °C or less.

[0085] Such a first substance employed herein can be an Au-Ag-Sn alloy (for example, composition ratio: Au-5.7 atomic % Ag-82 atomic % Sn, melting point: about 240 °C), an Au-Ga-Sn alloy (for example, composition ratio: Au-10 atomic % Ga-18 atomic % Sn, melting point: about 260 °C), etc., which exhibit an oxygen-bonding energy of 500 kJ or more. Here, the oxygen-bonding energies are approximately Au: 30 kJ, Ag: 130 kJ, Sn: 610 kJ and Ga: 740 kJ.

[0086] The first layer employed herein can be an In-48.3 atomic % Sn film. This layer has a melting point of 120 °C. The oxygen-bonding energies are about 640 kJ for In and about 610 kJ for Sn.

[0087] The second and third substances employed herein can be the same as those of the aforementioned First Preferred Embodiment.

[0088] Here, a variety of recording media are disclosed in the aforementioned conventional publications. Many of them, however, have recording films of low reflectance. Moreover, even when they have recording films in which Al of high reflectance is a major component, since Al of high reflectance is a major component in the recording portions, the reflectance at the recording portions is not reduced so much. Consequently, it is believed that they exhibit small modulations.

[0089] In substances which undergo an oxidation-reduction reaction, those which are of good reflectance exhibit small absorptance to the external energy, such as the laser beam, because they are of good reflectance. Consequently, it is believed that they absorb energies less which are required for the reaction. Therefore, it is necessary to make both of the substances a combination of good reactivity. Even if such is the case, both of the substances react, for example, in the formation of the recording film or when the external energy is not applied. Hence, there still is a large possibility of reducing the modulation.

[0090] Whereas, in the aforementioned preferred embodiment, the first and second substances are made into a combination of good reactivity by controlling the oxygen-bonding energy, the oxygen-dissociating energy, etc. It is possible, however, to suppress the reaction between the first and second substances, reaction which degrades the recording characteristics other than the case where information is recorded, by the interposing third substance (the hydrocarbon film 30 in the preferred embodiment). Accordingly, it is possible to exhibit modulations of favorable values (for example, as set forth in Fig. 2 and Fig. 3, 80% or more).

#### (Third Preferred Embodiment)

[0091] In the optical disk 100 illustrated in Fig. 1, this Third Preferred Embodiment differs from the recording medium of the aforementioned First Preferred Embodiment in that the first layer is an In-3.2 atomic % Ag film

400 instead of the Sn-10 atomic % Sr film, and in that the barrier layer is a Ti film 300 instead of the C film. The recording medium of this preferred embodiment operates and effects advantages in the substantially same manner as the recording medium of the aforementioned First Preferred Embodiment. Hereinafter, the portions, which differ from those of the recording medium of the First Preferred Embodiment, will be described mainly.

[0092] The manufacturing method of the recording medium of this preferred embodiment will be described with reference to a specific example.

[0093] On the surface 1b of the substrate 1, the WO<sub>3</sub> film 2 was formed in a thickness of 175 nm by an RF magnetron sputtering method with a WO<sub>3</sub> target under the following film forming conditions of sputtering gas species: Ar + 10% O<sub>2</sub>, sputtering gas pressure: 0.533 Pa (4 x 10<sup>-3</sup> Torr) and input electric power: 100 - 400 W.

[0094] Subsequently, the Ti film 300 was formed in a thickness of 1 nm by an RF magnetron sputtering method with a Ti target under the following film forming conditions of sputtering gas species: Ar, sputtering gas pressure: 0.533 Pa (10<sup>-3</sup> Torr) and input electric power 100 - 200 W.

[0095] Still subsequently, the In-3.2 atomic % Ag film 400 was formed in a thickness of 45 nm by an RF magnetron sputtering method with an In-3.2 atomic % Ag target under the following film forming conditions of sputtering gas species: Ar, sputtering gas pressure: 0.533 Pa (4 x 10<sup>-3</sup> Torr) and input electric power: 50 - 200 W.

[0096] Finally, the ultraviolet-curable resin was applied by a spin coating method. The ultraviolet-curable resin was cured using a high-pressure mercury-vapor lamp to form the resin film 5. Thus, the optical disk 100 was manufactured.

[0097] The recording actions of the optical disk 100 according to this preferred embodiment are assumed to be as follows. In the portion of the guide groove 1c, the recording laser beam enters (irradiates) in the direction of the arrow "A", and is focused on the surface of the In-3.2 atomic % Ag film 400. Since the melting point of the In-3.2 atomic % Ag is as low as about 141 °C, a part of or all of the In-3.2 atomic % Ag film 400, which is irradiated with the laser beam, melts. In a certain case, holes are formed in the In-3.2 atomic % Ag film 400 in this instance.

[0098] Simultaneously therewith, the WO<sub>3</sub> film 2 and the In-3.2 atomic % Ag film 400, a part of or all of which melts, undergo a chemical reaction with the WO<sub>3</sub> and the In-3.2 atomic % Ag passing through the Ti film 300 and/or destroying the Ti film 300. Accordingly, the optical characteristics (reflectance, etc.) of the recording film vary so that information can be recorded. Since the chemical reaction occurs between the molten liquid and the solid, the reaction occurs more easily than the case where the reaction occurs between a solid and the other solid.

[0099] When the recording laser beam is not irradiat-

ed, since the Ti film 300 is interposed between the  $WO_3$  film and the In-3.2 atomic % Ag film 400, the reaction between the  $WO_3$  film 2 and the In-3.2 atomic % Ag film 400 is suppressed. As a result, the recording characteristics can be inhibited from degrading.

[0100] The reaction between the  $WO_3$  film 2 and the In-3.2 atomic % Ag film 400 herein is also an oxidation-reduction reaction in a wide sense as hereinafter described. By irradiating with the recording laser beam, the  $WO_3$ , forming the film 2, is reduced, and a part of or all of it is turned into  $WO_{2.83}$ . The In-3.2 atomic % Ag, forming the film 400, is oxidized, and mainly a part of or all of In is chiefly turned into  $In_2O_{3-x}$ .

[0101] At this moment, the color hues of the substances constituting the films are as follows. The  $WO_3$  is transparent, the  $WO_{2.83}$  is blue, the In-3.2 atomic % Ag is metallic gloss, and the  $In_2O_{3-x}$  is black. Accordingly, the optical characteristics of the optical disk 100 before and after recording vary greatly.

[0102] The energy required for the  $WO_3$  to dissociate oxygen molecules in an amount of 1 mol and to turn into the  $WO_{2.83}$  (oxygen-dissociating energy) is about 480 kJ at room temperature. The energy generated by the In to bond with oxygen molecules in an amount of 1 mol and to turn into the  $In_2O_{3-x}$  (oxygen-bonding energy) is about 640 kJ at room temperature. Here, the oxygen-bonding energy required for Ag to turn into  $Ag_2O$  is about 130 kJ at room temperature.

[0103] This preferred embodiment also exhibits the same recording action in the same manner as that of the aforementioned Second Preferred Embodiment. Moreover, in this preferred embodiment as well, since the aforementioned oxidation-reduction reaction is an exothermic reaction, the modified reaction products ( $WO_{2.83}$  and  $In_2O_{3-x}$ ) are stable energetically, and the reverse reaction is less likely to occur. In addition, since the substances before the generation or after the generation are the oxides or the substance containing oxygen as a constituent element, they are strong against heat and moisture, etc., and are good in environmental resistance. Thus, when information is not recorded, it is likely to suppress the unnecessary reactions.

[0104] In the optical disk 100, information was recorded by irradiating with a laser beam (recording laser beam) of wavelength: 780 nm from the side of the flat surface (surface 1a), which was focused on the surface of the In-3.2 atomic % Ag film 400 through an objective lens of NA (numerical aperture): 0.5. At this moment, the irradiating conditions were linear velocity: 2.8 m/sec, recording frequency: 400 kHz and recording laser wave form: rectangular wave of 50% duty ratio. The characteristics (recording characteristics) of the optical disk in this instance were, as set forth in Fig. 4, reflectance at unrecorded portions: 63%, recording laser power: 7 mW, C/N: 52 dB and modulation: 93%.

[0105] Then, the optical disk characteristics as set forth above were measured by variously changing the thickness of the Ti film 300 playing the role of the barrier

layer (Sample Nos. 21 and 23), and Fig. 4 summarizes the results, together with the aforementioned results (Sample No. 22). Note that, in Fig. 4, Sample No. 24 was a comparative example to the present invention, and was free from the barrier layer.

[0106] As set forth in Fig. 4, it is understood that the optical disks 100 of this preferred embodiment listed as Sample Nos. 21 through 23 exhibited remarkably higher reflectance than the optical disk of the comparative example (Sample No. 24), and that they were well balanced in terms of the characteristics, such as the reflectance, the recording power, the C/N and the modulation. This results from the arrangement that the reaction between the first layer, the In-3.2 atomic % Ag film 400, and the second layer, the  $WO_3$  film 2, is suppressed especially in the formation of the films.

[0107] Moreover, the respective optical disks of Sample Nos. 21 through 24 were subjected to an environmental resistance test which was carried out at 55 °C for 96 hours. The optical disks of this preferred embodiment could read out the recorded data. Whereas, it was impossible for the optical disk of the comparative example to read out the recorded data. This results from the arrangement that the reaction between the  $WO_3$  film 2 and the In-3.2 atomic % Ag film 400 is suppressed by the presence of the Ti film 300.

[0108] As described so far, the optical disks this preferred embodiment are characterized in that they are better balanced in terms of the characteristics, such as the reflectance, the recording power, the C/N and the modulation, than the conventional optical disk.

[0109] Moreover, in this preferred embodiment, since the Ti film 300 is interposed between the  $WO_3$  film 2 and the In-3.2 atomic % Ag film 400, the reaction is suppressed in the formation of the films, under ordinary environment, and under the high-temperature-and-high humidity conditions such as the aforementioned environmental resistance test. Thus, the reflectance (initial reflectance) at the unrecorded portions of the optical disk can be heightened remarkably. In addition, the recording characteristics (reflectance, recording powder, C/N and modulation) can be inhibited from degrading, and the data retention characteristic can be improved greatly.

[0110] Note that the metal employed as the barrier layer (Ti film 300 in this preferred embodiment) can preferably exhibit a thermal diffusion coefficient of 50 mm<sup>2</sup>/sec or less in bulk. When the metal exhibits a thermal diffusion coefficient of 50 mm<sup>2</sup>/sec or more, a laser beam power, which is applied when recording information, should be increased. Accordingly, such a metal is not so practical for a recording medium. Also note that, in the Ti film 300 employed as the barrier layer in this preferred embodiment, Ti exhibits a thermal diffusion coefficient value of about 9.3 mm<sup>2</sup>/sec in bulk (at room temperature), that Ti generates an energy of about 1,070 kJ when it bonds with oxygen molecules in an amount of 1 mol, and that Ti has a melting point of 1,675

°C.

[0111] Further, in the aforementioned optical disk 100, the first, second and third layers, constituting the recording film, cannot necessarily consist of the first, second and third substances only, respectively. The first, second and third substances can be mixed with other substances to form the respective layers.

[0112] Furthermore, the optical disk can comprise a laminated construction of the first layer and the second layer; the first layer can be constituted by the third substance coexisting with one of the first substance and the second substance; and the second layer can comprise the other one of the first substance and the second substance which is not contained in the first layer.

[0113] Moreover, the recording film cannot necessarily be the aforementioned laminated construction. It can be a single-layered construction in which the third substance interposes between the first and second substances in one layer. In addition, since the major portion of the present invention exists in the recording film, the constituent elements other than the recording film can be designed alternatively at one's discretion.

[0114] Whilst, the recording medium, to which the present invention is applied, is not limited to the form of the aforementioned optical disk, but can have other forms. Additionally, the external energy, which induces the reaction to vary the optical characteristics, is not limited to the laser beam, but can be light in general, heat, electromagnetic wave, sound wave, radiation, impact force, strain, etc. For example, the present invention can be applied to a thermo label, or the like, in which the first substance and the second substance undergo an oxidation-reduction reaction at a predetermined temperature to vary the optical characteristics so that information is recorded.

#### Claims

1. A recording medium, for recording information by varying optical characteristics thereof by applying an external energy thereto, characterised in that the recording medium comprises:
  - a first substance and a second substance which cause an exothermic reaction to vary optical characteristics of said first and second substances when the external energy is applied, said first substance undergoing oxidation in a wide sense, and said second substance undergoing reduction in a wide sense; and
  - a third substance interposed between said first substance and said second substance, enabling said first substance and said second substance to react when said external energy is applied, and suppressing said first substance and said second substance to react when said external energy is not applied.
2. The recording medium according to claim 1, wherein said second substance is at least one member selected from the group consisting of oxides, substances containing oxygen as a constituent element, substances with oxygen adsorbed and compounds or mixtures thereof, preferably wherein said second substance requires an energy of 550 kJ or less when dissociating oxygen molecules in an amount of 1 Mole.
3. The recording medium according to claim 1 or claim 2, wherein said second substance is a substance containing at least one member selected from the group consisting of oxides and substances containing oxygen as a constituent element, said members containing at least one element selected from the group consisting of elements of group 6 of the periodic table of the elements, elements of group 8 of the periodic table of the elements, elements of group 9 of the periodic table of the elements, elements of group 11 of the periodic table of the elements, Ti, V, Mn, Ni, Re, Ge, Sn, Pb, As, Sb, Bi, Se, Te, Ce, Pr and Tb, preferably wherein said second substance is at least one oxide selected from the group consisting of  $\text{MoO}_3$ ,  $\text{ReO}_2$ ,  $\text{PrO}_2$  and  $\text{SbO}_2$  or wherein said second substance is  $\text{WO}_3$ .
4. The recording medium according to any of claims 1 to 3, wherein said first substance is at least one member selected from the group consisting of metals, intermetallic compounds, nitrides, carbides, silicides, borides, sulfides, selenides, tellurides, phosphides, arsenides, antimonides and substances containing these members, the members generating an energy of 1.000 kJ or more when bonding with oxygen molecules in an amount of 1 Mole.
5. The recording medium according to claim 4, wherein said first substance is at least one member selected from the group consisting of Sn-Sr alloys, Mg-Al alloys, In-Sr alloys and Al-Ti alloys, preferably wherein said first substance is an Sn-10 atomic % Sr alloy.
6. The recording medium according to any of claims 1 to 3, wherein said first substance contains at least one member selected from the group consisting of metals, intermetallic compounds, nitrides, carbides, silicides, borides, sulfides, selenides, tellurides, phosphides, arsenides, antimonides and substances containing these members, which are generating an energy of 500 kJ or more when bonding with oxygen molecules in an amount of 1 Mole and exhibiting a melting point or a decomposition temperature of from 100 °C to 300 °C.
7. The recording medium according to claim 6, wherein said first substance is at least one member se-

- lected from the group consisting of Au-Ag-Sn alloys, Au-Ga-Sn alloys and In-Sn alloys, preferably wherein said first substance is an Sn-43 atomic % Bi alloy.
8. The recording medium according to any of claims 1 to 7, wherein said third substance is at least one member selected from the group consisting of oxides, substances containing oxygen as a constituent element, substances with oxygen adsorbed and compounds thereof or mixtures containing these members, which are generating a quantity of heat in excess of 550 kJ when dissociating oxygen molecules in an amount of 1 Mole, preferably wherein said oxide is  $Al_2O_3$  or  $SiAlON$ .
9. The recording medium according to any of claims 1 to 7, wherein said third substance is an organic substance which exhibits a decomposition temperature, sublimation temperature or melting temperature of 300 °C or less, preferably wherein said organic substance is  $C_mH_n$  (hydrocarbon),  $C_mF_n$  or  $C_mH_nF_p$  (m, n and p are integers).
10. The recording medium according to any of claims 1 to 7, wherein said third substance is a substance including at least one member selected from the group consisting of metals, such as Mn, Ti, Se, Mn steels, titanium alloys, Si, Ge or  $SiN_x$ , semiconductors, intermetallic compounds, nitrides, carbides, silicides, borides, sulfides, selenides, tellurides, phosphides, arsenides, antimonides and substances containing these members, which are exhibiting a thermal diffusion coefficient of 50 mm<sup>2</sup>/s or less in bulk at room temperature.
11. The recording medium according to any of claims 1 to 7, wherein said third substance is carbon or a hydrocarbon resin or titanium.
12. The recording medium according to any of claims 1 to 11, wherein said first substance, said second substance and said third substance are formed as a layer, respectively, and are laminated with a layer including the third substance in the middle.
13. The recording medium according to any of claims 1 to 7, wherein the third substance exhibits a melting point, a decomposition temperature or a sublimation temperature of 1.000 °C or more in the case where the third substance generates an energy of 1.000 kJ or more when bonding with oxygen molecules in an amount of 1 Mole, or exhibits a melting point, a decomposition temperature or a sublimation temperature of 300 °C or more in the case where the third substance generates an energy of less than 1.000 kJ when bonding with oxygen molecules in an amount of 1 Mole.
14. The recording medium according to any of claims 1 to 13, wherein said third substance is in a form of a layer, and has a thickness of 0,5 nm or more.

#### Patentansprüche

- Ein Aufzeichnungsmedium zum Aufzeichnen von Informationen durch Variieren von optischen Eigenschaften des Aufzeichnungsmediums durch Anwenden einer externen Energie auf das Aufzeichnungsmedium, **dadurch gekennzeichnet, dass** das Aufzeichnungsmedium umfasst:
  - eine erste Substanz und eine zweite Substanz, die eine exotherme Reaktion zum Variieren von optischen Eigenschaften der ersten und der zweiten Substanz verursachen, wenn die externe Energie angewandt wird, wobei die erste Substanz einer Oxidation im weiteren Sinn unterliegt und die zweite Substanz einer Reduktion im weiteren Sinn unterliegt; und
  - eine dritte Substanz, die zwischen der ersten Substanz und der zweiten Substanz angeordnet ist, welche die erste Substanz und die zweite Substanz reagieren lässt, wenn die externe Energie angewandt wird, und welche die Reaktion der ersten und der zweiten Substanz unterdrückt, wenn die externe Energie nicht angewandt wird.
- Aufzeichnungsmedium nach Anspruch 1, bei dem die zweite Substanz mindestens ein Stoff ist, der aus der Gruppe bestehend aus Oxiden, Substanzen, die Sauerstoff als Bestandteil enthalten, Substanzen mit absorbiertem Sauerstoff und Verbindungen oder Gemischen davon ausgewählt ist, wobei vorzugsweise die zweite Substanz bei der Dissoziation von Sauerstoffmolekülen in einer Menge von 1 mol eine Energie von 550 kJ oder weniger erfordert.
- Aufzeichnungsmedium nach Anspruch 1 oder 2, bei dem die zweite Substanz eine Substanz ist, die mindestens einen Stoff enthält, der aus der Gruppe bestehend aus Oxiden und Substanzen ausgewählt ist, die Sauerstoff als Bestandteil enthalten, wobei die Stoffe mindestens ein Element enthalten, das aus der Gruppe bestehend aus Elementen der Gruppe 6 des PSE, Elementen der Gruppe 8 des PSE, Elementen der Gruppe 9 des PSE, Elementen der Gruppe 11 des PSE, Ti, V, Mn, Ni, Re, Ge, Sn, Pb, As, Sb, Bi, Se, Te, Ce, Pr und Tb ausgewählt ist, wobei vorzugsweise die zweite Substanz mindestens ein Oxid ist, das aus der Gruppe bestehend aus  $MoO_3$ ,  $ReO_2$ ,  $PrO_2$  und  $SbO_2$  ausgewählt ist oder wobei die zweite Substanz  $WO_3$  ist.

4. Aufzeichnungsmedium nach einem der Ansprüche 1 bis 3, bei dem die erste Substanz mindestens ein Stoff ist, der aus der Gruppe bestehend aus Metallen, intermetallischen Verbindungen, Nitriden, Carbiden, Siliciden, Boriden, Sulfiden, Seleniden, Telluriden, Phosphiden, Arseniden, Antimoniden und Substanzen ausgewählt ist, welche diese Stoffe enthalten, wobei die Stoffe bei der Bindung mit Sauerstoffmolekülen in einer Menge von 1 mol eine Energie von 1000 kJ oder mehr erzeugen. 5 10
5. Aufzeichnungsmedium nach Anspruch 4, bei dem die erste Substanz mindestens ein Stoff ist, der aus der Gruppe bestehend aus Sn-Sr-Legierungen, Mg-Al-Legierungen, In-Sr-Legierungen und Al-Ti-Legierungen ausgewählt ist, wobei vorzugsweise die erste Substanz eine Sn-10 Atom-% Sr-Legierung ist. 15
6. Aufzeichnungsmedium nach einem der Ansprüche 1 bis 3, bei dem die erste Substanz mindestens einen Stoff enthält, der aus Metallen, intermetallischen Verbindungen, Nitriden, Carbiden, Siliciden, Boriden, Sulfiden, Seleniden, Telluriden, Phosphiden, Arseniden, Antimoniden und Substanzen ausgewählt ist, welche diese Stoffe enthalten, die bei der Bindung mit Sauerstoffmolekülen in einer Menge von 1 mol eine Energie von 500 kJ oder mehr erzeugen und einen Schmelzpunkt oder eine Zersetzungstemperatur von 100°C bis 300°C aufweisen. 20 25 30
7. Aufzeichnungsmedium nach Anspruch 6, bei dem die erste Substanz mindestens ein Stoff ist, der aus der Gruppe bestehend aus Au-Ag-Sn-Legierungen, Au-Ga-Sn-Legierungen und In-Sn-Legierungen ausgewählt ist, wobei vorzugsweise die erste Substanz eine Sn-43 Atom-% Bi-Legierung ist. 35
8. Aufzeichnungsmedium nach einem der Ansprüche 1 bis 7, bei dem die dritte Substanz mindestens ein Stoff ist, der aus der Gruppe bestehend aus Oxiden, Substanzen, die Sauerstoff als Bestandteil enthalten, Substanzen mit absorbiertem Sauerstoff und deren Verbindungen oder Gemischen ausgewählt ist, welche diese Stoffe enthalten, die bei der Dissoziation von Sauerstoffmolekülen in einer Menge von 1 mol eine Wärmemenge von mehr als 550 kJ erzeugen, wobei vorzugsweise das Oxid  $\text{Al}_2\text{O}_3$  oder  $\text{SiAlON}$  ist. 40 45 50
9. Aufzeichnungsmedium nach einem der Ansprüche 1 bis 7, bei dem die dritte Substanz eine organische Substanz ist, die eine Zersetzungstemperatur, eine Sublimationstemperatur oder eine Schmelztemperatur von 300°C oder weniger aufweist, wobei vorzugsweise die organische Substanz  $\text{C}_m\text{H}_n$  (Kohlenwasserstoff),  $\text{C}_m\text{F}_n$  oder  $\text{C}_m\text{H}_n\text{F}_p$  ist (wobei m, n und p ganze Zahlen sind). 55
10. Aufzeichnungsmedium nach einem der Ansprüche 1 bis 7, bei dem die dritte Substanz eine Substanz ist, die mindestens einen Stoff umfasst, der aus der Gruppe bestehend aus Metallen wie Mn, Ti, Se, Mn-Stählen, Titanlegierungen, Si, Ge,  $\text{SiN}_x$ , usw., Halbleitern, intermetallischen Verbindungen, Nitriden, Carbiden, Siliciden, Boriden, Sulfiden, Seleniden, Telluriden, Phosphiden, Arseniden, Antimoniden und Substanzen ausgewählt ist, welche diese Stoffe enthalten, die als Masse einen thermischen Diffusionskoeffizienten von 50  $\text{mm}^2/\text{s}$  oder weniger bei Raumtemperatur aufweisen.
11. Aufzeichnungsmedium nach einem der Ansprüche 1 bis 7, bei dem die dritte Substanz Kohlenstoff oder ein Kohlenwasserstoffharz oder Titan ist.
12. Aufzeichnungsmedium nach einem der Ansprüche 1 bis 11, bei dem die erste Substanz, die zweite Substanz und die dritte Substanz jeweils als Schicht ausgebildet sind und mit einer Schicht, welche die dritte Substanz umfasst, in der Mitte laminiert sind.
13. Aufzeichnungsmedium nach einem der Ansprüche 1 bis 7, bei dem die dritte Substanz einen Schmelzpunkt, eine Zersetzungstemperatur oder eine Sublimationstemperatur von 1000°C oder mehr in dem Fall aufweist, bei dem die dritte Substanz bei der Bindung mit Sauerstoffmolekülen in einer Menge von 1 mol eine Energie von 1000 kJ oder mehr erzeugt, oder einen Schmelzpunkt, eine Zersetzungstemperatur oder eine Sublimationstemperatur von 300°C oder mehr in dem Fall aufweist, bei dem die dritte Substanz bei der Bindung mit Sauerstoffmolekülen in einer Menge von 1 mol eine Energie von weniger als 1000 kJ erzeugt.
14. Aufzeichnungsmedium nach einem der Ansprüche 1 bis 13, bei dem die dritte Substanz in Form einer Schicht vorliegt und eine Dicke von 0,5 nm oder mehr aufweist.

#### Revendications

1. Support d'enregistrement pour enregistrer des informations faisant varier les caractéristiques optiques de celui-ci en lui appliquant une énergie externe, caractérisé en ce que le support d'enregistrement comprend :
- une première substance et une deuxième substance qui provoquent une réaction exothermique pour faire varier les caractéristiques optiques de ladite première substance et de la-

- dite deuxième substance quand on applique l'énergie externe, la première substance subissant une oxydation au sens large, et ladite deuxième substance subissant une réduction au sens large ; et
- une troisième substance interposée entre ladite première substance et ladite deuxième substance, permettant à ladite première substance et à ladite deuxième substance de réagir lorsqu'on applique ladite énergie externe, et supprimant la réaction de ladite première substance et de ladite deuxième substance lorsque l'énergie externe n'est pas appliquée.
2. Support d'enregistrement selon la revendication 1, dans lequel ladite deuxième substance est au moins un élément choisi parmi le groupe comprenant les oxydes, les substances contenant de l'oxygène à titre d'élément constitutif, les substances avec de l'oxygène adsorbé, ainsi que les composés ou les mélanges de ces derniers, de préférence dans lequel ladite deuxième substance exige une énergie de 550 kJ ou moins lorsqu'on dissocie les molécules d'oxygène en quantité de 1 mole.
  3. Support d'enregistrement selon l'une ou l'autre des revendications 1 et 2, dans lequel ladite deuxième substance est une substance qui contient au moins un élément choisi parmi le groupe constitué des oxydes et des substances contenant de l'oxygène à titre d'élément constitutif, lesdits éléments contenant au moins un élément choisi parmi le groupe constitué des éléments du groupe 6 du tableau périodique des éléments, des éléments du groupe 8 du tableau périodique des éléments, des éléments du groupe 9 du tableau périodique des éléments, des éléments du groupe 11 du tableau périodique des éléments, Ti, V, Mn, Ni, Re, Ga, Sn, Pb, As, Sb, Bi, Se, Te, Ce, Pr et Tb, et de préférence dans lequel ladite deuxième substance est au moins un oxyde choisi parmi le groupe constitué de  $\text{MoO}_3$ ,  $\text{ReO}_2$ ,  $\text{PrO}_2$  et  $\text{SbO}_2$ , ou dans lequel ladite deuxième substance est  $\text{WO}_3$ .
  4. Support d'enregistrement selon l'une quelconque des revendications 1 à 3, dans lequel ladite première substance est au moins un élément choisi parmi le groupe constitué des métaux, des composés intermétalliques, des nitrures, des carbures, des siliciures, des borures, des sulfures, des séléniures, des tellures, des phosphures, des arséniures, des antimoniures et des substances comprenant ces éléments, lesdits éléments engendrant une énergie de 1000 kJ ou plus lorsqu'ils s'associent avec les molécules d'oxygène en quantité de 1 mole.
  5. Support d'enregistrement selon la revendication 4, dans lequel ladite première substance est au moins un élément choisi parmi le groupe comprenant les alliages Sn-Sr, les alliages Mg-Al, les alliages In-Sr et les alliages Al-Ti, et de préférence dans lequel ladite première substance est un alliage de Sn et de 10 atomes % de Sr.
  6. Support d'enregistrement selon l'une quelconque des revendications 1 à 3, dans lequel ladite première substance contient au moins un élément choisi parmi le groupe constitué des métaux, des composés intermétalliques, des nitrures, des carbures, des siliciures, des borures, des sulfures, des séléniures, des tellures, des phosphures, des arséniures, des antimoniures, et des substances contenant ces éléments, qui présentent généralement une énergie de 500 kJ ou plus lorsqu'ils s'associent avec des molécules d'oxygène en quantité de 1 mole, et présentant un point de fusion ou une température de décomposition de 100 à 300°C.
  7. Support d'enregistrement selon la revendication 6, dans lequel ladite première substance est au moins un élément choisi parmi le groupe constitué des alliages Au-Ag-Sn, des alliages Au-Ga-Sn et des alliages In-Sn, et de préférence dans lequel ladite première substance est un alliage de Sn avec 43 atomes % de Bi.
  8. Support d'enregistrement selon l'une quelconque des revendications 1 à 7, dans lequel ladite troisième substance est au moins un élément choisi parmi le groupe constitué des oxydes, des substances contenant de l'oxygène à titre d'élément constitutif, des substances avec de l'oxygène adsorbé et leurs composés ou des mélanges contenant ces éléments, qui engendrent une quantité de chaleur dépassant 550 kJ lorsqu'on dissocie les molécules d'oxygène en quantité de 1 mole, et de préférence dans lequel ledit oxyde est  $\text{Al}_2\text{O}_3$ , ou  $\text{SiAlON}$ .
  9. Support d'enregistrement selon l'une quelconque des revendications 1 à 7, dans lequel ladite troisième substance est une substance organique qui présente une température de décomposition, une température de sublimation ou une température de fusion de 300°C ou moins, et de préférence dans lequel ladite substance organique est  $\text{C}_m\text{H}_n$  (hydrocarbures),  $\text{C}_m\text{F}_n$ ,  $\text{C}_m\text{H}_n\text{F}_p$  (m, n et p étant des entiers).
  10. Support d'enregistrement selon l'une quelconque des revendications 1 à 7, dans lequel ladite troisième substance est une substance qui inclut au moins un élément choisi parmi le groupe constitué des métaux, comme des aciers au Mn, Ti, Se, Mn, des alliages de titane, du Si, Ge ou  $\text{SiN}_x$ , des semi-conducteurs, des composés intermétalliques, des

nitrides, des carbures, des siliciures, des borures, des sulfures, des sélénures, des tellures, des phosphures, des arsénures, des antimoniures et des substances contenant ces éléments, qui présente un coefficient de diffusion thermique de 50 mm<sup>2</sup>/seconde ou moins en vrac à température ambiante.

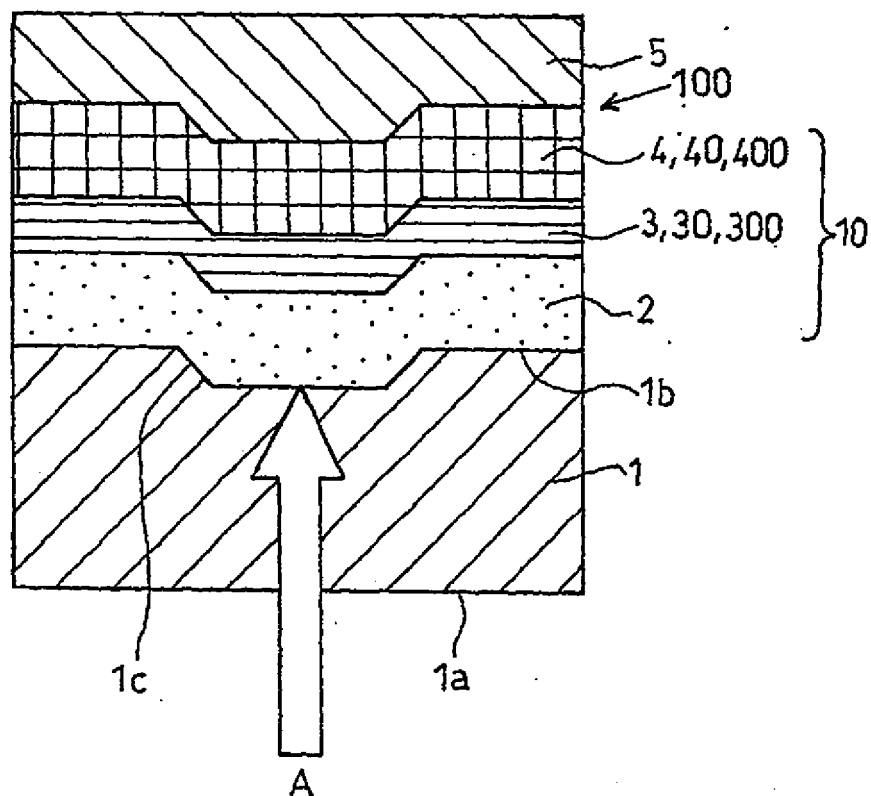
11. Support d'enregistrement selon l'une quelconque des revendications 1 à 7, dans lequel ladite troisième substance est du carbone, ou une résine d'hydrocarbures, ou du titane. 5 10
12. Support d'enregistrement selon l'une quelconque des revendications 1 à 11, dans lequel ladite première substance, ladite deuxième substance et ladite troisième substance sont formées respectivement par une couche, et celles-ci sont stratifiées avec une couche qui inclut la troisième substance au milieu. 15 20
13. Support d'enregistrement selon l'une quelconque des revendications 1 à 7, dans lequel la troisième substance présente un point de fusion, une température de décomposition ou une température de sublimation, de 1.000°C ou plus dans le cas dans lequel la troisième substance engendre une énergie de 1000 kJ ou plus lorsqu'elle s'associe avec des molécules d'oxygène en quantité de 1 mole, ou présente un point de fusion, une température de décomposition ou une température de sublimation de 300°C ou plus dans le cas dans lequel la troisième substance engendre une énergie inférieure à 1000 kJ lorsqu'elle s'associe avec des molécules d'oxygène en quantité de 1 mole. 25 30 35
14. Support d'enregistrement selon l'une quelconque des revendications 1 à 13, dans lequel ladite troisième substance est sous la forme d'une couche, et présente une épaisseur de 0,5 nm ou plus. 40

45

50

55

FIG. 1



- 1: SUBSTRATE
- 2: WO<sub>3</sub> FILM
- 3: C FILM
- 4: Sn-10 ATOMIC% Sr FILM
- 10: RECORDING FILM
- 100: OPTICAL DISK



Fig. 2

Sample No.	Barrier Layer Reflectance at Thickness	Unrecorded Portions	Recording Laser Power	C/N	Modulation
1	0.5 nm	52%	9 mW	48 dB	85%
2	1 nm	60%	10 mW	50 dB	85%
3	2 nm	62%	10 mW	50 dB	80%
4	3 nm	61%	10 mW	50 dB	80%
5	5 nm	58%	11 mW	50 dB	85%
6	0 nm	42%	8 mW	47 dB	80%
(Comp. Ex.)					

Fig. 3

Sample No.	Barrier Layer Reflectance at Thickness	Unrecorded Portions	Recording Laser Power	C/N	Modulation
11	1 nm	60%	6 mW	51 dB	85%
12	2 nm	63%	7 mW	52 dB	85%
13	3 nm	62%	7 mW	52 dB	85%
14 (Comp. Ex.)	0 nm	45%	6 mW	50 dB	80%

Fig. 4

Sample No.	Barrier Layer Reflectance at Thickness	Unrecorded Portions	Recording Laser Power	C/N	Modulation
21	0.5 nm	63%	7 mW	52 dB	92%
22	1 nm	63%	7 mW	52 dB	93%
23	2 nm	62%	8 mW	53 dB	93%
24 (Comp. Ex.)	0 nm	40%	6 mW	50 dB	90%